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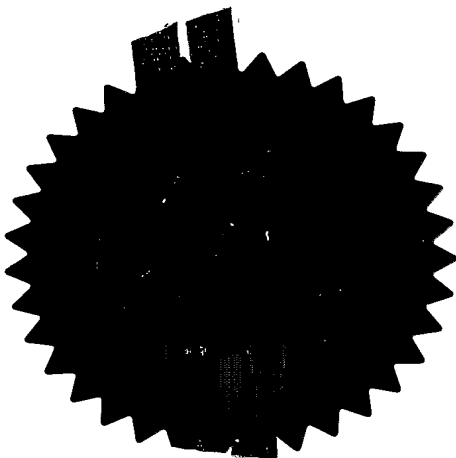
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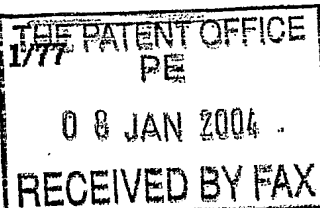


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## 3. Full name, address and postcode of the or of each applicant (underline all surnames)

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Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

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7236326001

## 4. Title of the invention

ELECTRO-CHEMICAL SENSOR

## 5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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01223 325268

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DUPLICATE

### Electro-chemical Sensor

The invention relates to a chemical sensor tool for use in downhole and methods for analyzing of fluids produced from subterranean formations. More specifically it relates to a electro-chemical sensor for downhole pH and ion content analysis of effluents produced from subterranean formation.

### BACKGROUND OF THE INVENTION

10

Analyzing samples representative of downhole fluids is an important aspect of determining the quality and economic value of a hydrocarbon formation.

15 Present day operations obtain an analysis of downhole fluids usually through wireline logging using a formation tester such as the MDT™ tool of Schlumberger Oilfield Services. However, more recently, it was suggested to analyze downhole fluids either through sensors permanently or quasi-permanently  
20 installed in a wellbore or through sensor mounted on the drillstring. The latter method, if successfully implemented, has the advantage of obtaining data while drilling, whereas the former installation could be part of a control system for wellbores and hydrocarbon production therefrom.

25

To obtain an estimate of the composition of downhole fluids, the MDT tools uses an optical probe to estimate the amount of hydrocarbons in the samples collected from the formation. Other sensors use resistivity measurements to discern various  
30 components of the formations fluids.

Particularly, knowledge of downhole formation (produced) water chemistry is needed to save costs and increase production at all stages of oil and gas exploration and production. Knowledge of

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particularly the water chemistry is important for a number of key processes of the hydrocarbon production, including:

- Prediction and assessment of mineral scale and corrosion;
- 5 -Strategy for oil/water separation and water re-injection;
- Understanding of reservoir compartmentalization / flow units;
- Characterization of water break-through;
- Derivation of the water cut  $R_w$  ;and
- Evaluation of downhole the  $H_2S$  partition the oil and or water
- 10 (if used for  $H_2S$  measurements).

Some chemical species dissolved in water (like, for example,  $Cl^-$  and  $Na^+$ ) do not change their concentration when removed to the surface either as a part of a flow through a well, or as a

15 sample taken downhole. Consequently information about their quantities may be obtained from downhole samples and in some cases surface samples of a flow. However, the state of chemical species, such as  $H^+$  ( $pH = -\log[\text{concentration of } H^+]$ ),  $CO_2$ , or  $H_2S$  may change significantly while tripping to the surface. The

20 change occurs mainly due to a difference in temperature and pressure between downhole and surface environment. In case of sampling, this change may also happen due to degassing of a sample (seal failure), mineral precipitation in a sampling bottle, and (especially in case of  $H_2S$ ) - a chemical reaction

25 with the sampling chamber. It should be stressed that  $pH$ ,  $H_2S$ , or  $CO_2$  are among the most critical parameters for corrosion and scale assessment. Consequently it is of considerable importance to have their downhole values precisely known.

30 The concentration of protons or its logarithm  $pH$  can be regarded as the most critical parameter in water chemistry. It determines the rate of many important chemical reactions as well as the solubility of chemical compounds in water, and (by extension) in hydrocarbon.

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Hence, there is and will continue to be a demand for downhole chemical measurements. However, no downhole chemical measurements actually performed in an oil and gas producing well have been reported so far, though many different methods and tools have been proposed in the relevant literature.

General downhole measurement tools for oilfield applications are known as such. Examples of such tools are found in the United States Patents Nos. 6,023,340; 5,517,024; and 5,351,532 or in the International Patent Application WO 99/00575. An example of a probe for potentiometric measurements of ground water reservoirs is further published as: Solodov, I.N., Velichkin, V.I., Zotov, A.V. et al. "Distribution and Geochemistry of Contaminated Subsurface Waters in Fissured Volcanogenic Bed Rocks of the Lake Karachai Area, Chelyabinsk, Southern Urals" in: Lawrence Berkeley Laboratory Report 36780/UC-603(1994b), RAC-6, Ca, USA.

The known state of the art in the field of high temperature potentiometric measurements and tool is described for example in the published UK patent application GB-2362469 A.

A number of chemical analysis tools are known from chemical laboratory practice. Such known analysis tools include for example the various types of chromatography, electrochemical and spectral analysis. Particularly, the potentiometric method has been widely used for the measurements of water composition (pH, Eh,  $H_2S$ ,  $CO_2$ ,  $Na^+$ ,  $Cl^-$  etc...) both in the laboratory and in the field of ground water quality control. US patent no 5,223,117 discloses a two-terminal voltammetric microsensor having an internal reference using molecular self-assembling to form a system in which the reference electrode and the indicator electrode are both on the sensor electrode. The reference molecule is described as a redox system that is pH-insensitive, while the indicator molecule is formed by a hydro-quinone based



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redox system having a potential that shifts with the pH. Both, reference molecule and indicator molecule layers are prepared by self-assembly on gold (Au) microelectrodes. In the known microsensor, a pH reading is derived from peak readings of the  
5 voltagrams.

The laboratory systems, however, are often not suitable for wellbore application with demands for ruggedness, stability and low maintenance and energy consumption being rarely met.

10

It is therefore an object of the present invention to provide apparatus and methods to perform electro-chemical measurements in hydrocarbon wells during drilling and production. More specifically, it is an object of the present invention to  
15 provide robust sensors for molecularly selective electro-chemical measurements, in particular pH measurements.

#### SUMMARY OF THE INVENTION

20 The invention achieves its objects by providing a electro-chemical sensor having an measuring electrode with at least two receptors sensitive to the same species.

A electro-chemical technique can be applied for example as part  
25 of a production logging tool and open hole formation tester tool (Modular Dynamic Tester, MDT). In the latter case, the technique can provide a downhole real-time water sample validation or downhole pH for prediction of mineral scale and corrosion assessment.

30

These and other features of the invention, preferred embodiments and variants thereof, possible applications and advantages will become appreciated and understood by those skilled in the art from the following detailed description and drawings.

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## BRIEF DESCRIPTION OF DRAWINGS

- FIG. 1 shows a schematic diagram of the main elements of a known voltametric sensor;
- 5
- FIG. 2 shows a schematic diagram of the main elements of a known electro-chemical microsensor and its operation;
- FIG. 3 shows a schematic diagram of a known downhole probe using potentiometric sensors;
- 10
- FIG. 4A illustrates the surface structure of a measuring electrode in accordance with an example of the invention;
- 15
- FIG. 4B illustrates the surface structure of a measuring electrode with internal reference electrode in accordance with another example of the invention;
- FIG. 4C illustrates the geometrical surface layout of the electrode of FIG. 4B;
- 20
- FIG. 5 is a perspective view, partially cut-away, of a sensor in accordance with an example of the present invention in a downhole tool;
- 25
- FIG. 6 show voltammograms recorded from an electro-chemical microsensor in accordance with the present invention at three different pH values;
- 30
- FIG. 7 illustrates the shift of the peak potential for anthraquinone ,diphenyl-p-phenylenediamine and a combination of the two redox systems;

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FIG. 8 illustrates an example of a sensor in accordance with the invention as part of a wireline formation testing apparatus in a wellbore;

5 FIG. 9 shows a wellbore and the lower part of a drill string including the bottom-hole-assembly, with a sensor in accordance with the invention; and

FIG. 10 shows a sensor located downstream of a venturi-type flowmeter, in accordance with the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

15 The theory of voltammetry and its application to surface water measurements at ambient temperatures are both well developed. The method is based on the measurement of the electromotive force (e.m.f.) or potential  $E$  in a potentiometric cell which includes measuring and reference electrodes (half-cells).

20

FIG. 1 shows the general components of a known voltammetric cell 10. A measuring electrode 11 is inserted into a solution 13. This electrode consists of an internal half element (for example, Ag wire covered by an AgCl salt) in a solution of a  
25 fixed pH (for example, 0.1M HCl in some pH electrodes), and an ion-selective membrane 111 (like glass  $H^+$  selective membrane in pH glass electrode). The reference electrode 12 also contains an internal half-element (typically the same AgCl/Ag) inserted in a concentrated KCl (For example 3M) solution / gel saturated with  
30  $Ag^+$ , which diffuses (or flows) through the reference (liquid) junction 121.

The ion-selective electrode 11 measures the potential that arises because of the difference in activity or concentration of  
35 a corresponding ion ( $H^+$  in case of pH) in the internal solution

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and in the measured solution. This potential is measured against the reference potential on the reference electrode 12, which is fixed because of a constant composition of a reference solution / gel. The electrodes may be separated (separate half cells), or  
5 combined into one ("combination electrode").

The measured e.m.f. is an overall function of the temperature and the activity of an  $i$ th ion, to which the measuring electrode is selective:

10

$$[1] \quad E = E^0 + (k \cdot T) \cdot \log(a_i),$$

where  $E$  is the measured electromotive force (e.m.f.) of the cell (all potentials are in V),  $a_i$  corresponds to the activity of the  
15  $i$ th ion and is proportional to its concentration.  $E^0$  is the standard potential (at temperature  $T$ ) corresponding to the  $E$  value in a solution with the activity of  $i$ th ion equal to one. The term in parenthesis is the so-called Nernstian slope in a plot of  $E$  as a function of  $\log(a_i)$ . This slope (or the constant  
20 " $k$ ") together with the cell (electrode) constant ( $E^0$ ) is experimentally determined via a calibration procedure using standard solutions with known activities of  $i$ th ion. For good quality undamaged electrodes this slope should be very close to the theoretical one, equal to  $(R \cdot T / F \cdot z)$ , where  $F$  is the Faraday  
25 constant (23061 cal/mole),  $R$  is the gas constant (1.9872 cal/mole K),  $z_i$  is the charge of  $i$ th ion.

The Nernst equation [1] can be rewritten for pH sensors, i.e.  $\log a(H^+)$  as

30

$$[2] \quad E_{0.5} = K - (2.303 RT/nF) \text{pH}$$

where  $E_{0.5}$  is the half-wave potential of the redox system involved,  $K$  is an arbitrary constant,  $R$  is the ideal gas

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constant,  $m$  is the number of protons and  $n$  is the number of electrons transferred in the redox reaction.

The microsensor of US patent no 5,223,117 is illustrated in FIG.

5 2. FIG. 2A. shows a schematic electro-chemical sensor with a counter electrode 21 and a relatively much smaller (by a factor of 1000) Au substrate 22 that carries two molecular species  $M$  and  $R$ . The  $R$  species forms an inert reference electrode, and species  $M$  is an indicator electrode with specific receptors or  
10 sensitivity for a third species  $L$ . The schematic linear sweep voltammogram in the upper half of FIG 2C shows the difference in the current peaks for the oxidization in the normal state. When the third species  $L$  binds to  $M$  (FIG. 2B), this difference  
15 increases as illustrated by the shift of peaks in the lower half of FIG. 2C, thus providing a measure for the concentration of  $L$  in the solution surrounding the sensor. In the context of the present invention, it is important to note that the  $R$  is specifically selected to be insensitive to the species  $L$ , e.g. pH.

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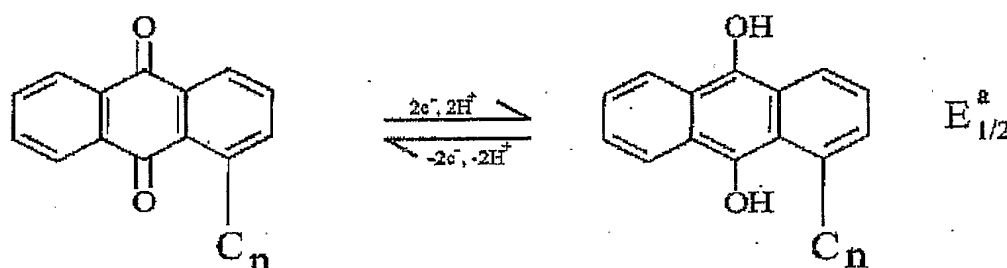
In FIG. 3, there are schematically illustrated elements of a known downhole analyzing tool 30 as used by Solodov et al (see background). The body of the tool 30 is connected to the surface via a cable 31 that transmits power and signals. A computer  
25 console 32 controls the tool, monitors its activity and records measurements. The tool 30 includes a sensor head with at number of selective electro-chemical probes 33 each sensitive to a different molecular species. Also housed in the body of the tool are further actuation parts 34 that operate the head, a test  
30 system 35 and transceivers 36 to convert measurements into a data stream and to communicate such data stream to the surface. The electrodes are located at the bottom part of the probe and include those for pH, Eh (or ORP),  $Ca^{2+}$  (pCa),  $Na^{+}$  (pNa),  $S^{2-}$  (pS),  $NH_4^{+}$  (pNH<sub>4</sub>), and reference electrode (RE).  $H_2S$  partial  
35 pressure may be calculated from pH and pS readings.

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In the following aspects and elements of the present invention are described in detail.

- 5 The present invention introduces a new molecular system in which the redox features of two molecules are combined, thus leading to a considerably higher accuracy and, in turn, downhole deployability.
- 10 In a preferred embodiment for a pH sensitive sensor an anthraquinone is homogenously derivatised onto carbon particles (AQC)



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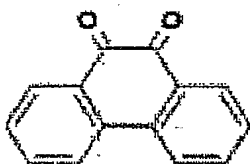
- The AQC system is derived using 2g of carbon powder (1.5  $\mu\text{m}$  in mean diameter) mixed with a 10  $\text{cm}^3$  solution containing 5 mM Fast Red AL Salt (Anthraquinone-1-diazonium chloride) to which 50 mM hypophosphorous acid (50%) is added. The reaction is allowed to
- 20 stand with occasional stirring at 5  $^\circ\text{C}$  for 30 minutes, after which it is filtered by water suction. Excess acid is removed by washing with distilled water and with the powder being finally washed with acetonitrile to remove any unreacted diazonium salt in the mixture. It is then air dried by placing inside a fume
- 25 hood for a period of 12 hours and finally stored in an airtight container.

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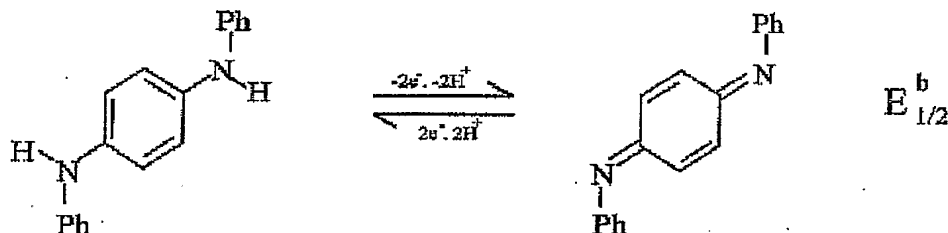
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In a similar manner, phenanthrenequinone (PAQ)



Is prepared as a second molecular species to undergo a redox reaction

Alternatively, N,N'-diphenyl-p-phenylenediamine (DPPD) spiked onto carbon particles undergoes a redox process as shown below:



The bonding of DPPD onto carbon is achieved by mixing 4 g of carbon powder with 25mL of 0.1M HCl + 0.1M KCl and 20mM DPPD solution in acetone. The reaction mixture is stirred continuously for 2 hours in a beaker and then filtered after which it was washed with distilled water to remove excess acid and chloride. It is then air dried by placing inside a fume hood for 12 hours and finally stored in an airtight container.

In a static environment where the sensor surface is not exposed to a flow, it is possible to immobilize water insoluble DPPD crystals directly onto the electrode surface. However in the wellbore environment it is preferred to link the sensitive molecules via a chemical bond to such surface.

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The derivatised carbon powders are abrasively immobilised onto a basal plane pyrolytic graphite (BPPG) electrode prior to voltammetric characterisation following a procedure described by Scholz, F. and Meyer, B., "Voltammetry of Solid Microparticles Immobilised on Electrode Surfaces in Electroanalytical Chemistry" ed. A.J. Bard, and I. Rubenstein, Marcel Dekker, New York, 1998, 20, 1. Initially the electrode is polished with glass polish paper (H00/240) and then with silicon carbide paper (P1000C) for smoothness. The derivatised carbons are first mixed and then immobilised onto the BPPG by gently rubbing the electrode surface on a fine qualitative filter paper containing the functionalised carbon particles.

The resulting modified electrode surfaces is schematically illustrated by FIG. 4A showing an electrode 41 with bonded DPPD and AQC.

It is further advantageous too add an internal pH reference involving a pH independent redox couple to increase the stability of any voltammetric reading, hence circumventing uncertainties caused by fouling of the external reference electrode. In the configuration, the sensor includes two reference electrodes.

A suitable reference molecule is, for example,  $K_3Mo(CN)_6$  or polyvinylferrocene (PVF) which both have a stable redox potential ( $K_3Mo(CN)_6$  at around 521 mV) that is sufficiently separated from expected shifting of redox signals of the two indicator species over the pH range of interest. As shown in Table 1 that both the oxidation and reduction potentials of  $K_3Mo(CN)_6$  are fairly constant across the entire pH range of interest.

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5 TABLE 1

pH	AQ <sub>ox</sub>	AQ <sub>red</sub>	DPPD <sub>ox</sub>	DPPD <sub>red</sub>	Mo <sup>-</sup> <sub>ox</sub>	Mo <sup>-</sup> <sub>red</sub>
4.6	0.440	0.448	0.202	0.224	0.524	0.524
6.8	0.576	0.580	0.094	0.082	0.528	0.522
9.2	0.710	0.674	0.204	-0.372	0.512	0.508

The Mo-based reference species can be retained in the solid substrate via ionic interactions with co-existing cationic polymer, such as poly (vinyl pyridine), that was spiked into the solid phase. Other pH independent species, such as ferrocyanide are less suitable as the redox peaks are obscured by the signals of the measuring redox system.

15

In FIG 4B the electrode 42 carries bonded molecules AQC and PAQ together with PVF as an internal reference molecule.

In FIG. 4C there is shown a possible geometric configuration or layout for the sensor surface 40 which is exposed to the wellbore fluid. The surface includes a working electrode 43 as described in FIGS. 4A or 4B, together with the (external) reference electrode 44 and a counter electrode 45.

A schematic of a microsensor 50 incorporating a modified surface prepared in accordance with the procedure described above is shown in FIG. 5. The body 51 of the sensor is fixed into the end section of an opening 52. The body carries the electrode surface

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511 and contacts 512 that provide connection points to voltage supply and measurement through a small channel 521 at the bottom of the opening 52. A sealing ring 513 protects the contact points and electronics from the wellbore fluid that passes under operation conditions through the sample channel 53.

It is an advantage of the new sensor to include two measuring or indicator electrodes or molecules measuring two e.m.f or potentials with reference to the same reference electrode and being sensitive to the same species or molecule in the environment. As a result the sensitivity towards a shift in the concentration of the species increases. Using the above example of AQC and DPPA and the pH (or  $H^+$  concentration, the Nernst equation applicable to the new sensor is the sum of the equations describing the individual measuring electrodes. Thus, combining the half wave potential  $E_{0.5}(AQC)$  for anthraquinone

$$[3] \quad E_{0.5}(AQC) = K(AQC) - (2.303 RT/nF)pH$$

with the half wave potential  $E_{0.5}(DPPD)$  for  $N,N'$ -diphenyl-p-phenylenediamine

$$[4] \quad E_{0.5}(DPPD) = K(DPPD) - (2.303 RT/nF)pH$$

yields the half wave potential  $E_{0.5}(S)$  for the combined system:

$$\begin{aligned} E_{0.5}(S) &= E_{0.5}(AQC) + E_{0.5}(DPPD) = \\ [5] \quad &(K(AQC) + K(DPPD)) - 2*(2.303 RT/nF)pH = \\ &K(S) - 2*(2.303 RT/nF)pH \end{aligned}$$

Where  $K(S)$  is the sum of the two constants  $K(AQC)$  and  $K(DPPD)$ . As the shift of the potential with a change in pH depends on the second term, the (theoretical) sensitivity of the sensor has doubled.

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The use of a further (third) redox system sensitive to the same species would in principle increase the sensitivity further. As the method detects shifts in the peak location of the voltammogram, however, more efforts are anticipated to be required to resolve overlapping peaks in such a three-molecule system.

FIG. 6 shows results in a range of pH solutions (pH 4.6, 0.1M acetic acid + 0.1M sodium acetate buffer; pH 6.8, 0.025M disodium hydrogen phosphate + 0.025M potassium dihydrogen phosphate buffer; pH 9.2, 0.05M disodium tetraborate buffer). The figure presents the corresponding square wave voltammograms when the starting potential was sufficiently negative to have both DPPD and AQ in their reduced forms.

15

FIG. 7 depicts the relationship between the redox potential and pH for both the DPPD (•) and AQ (•). The plot reveals a linear response from pH 4 to 9 with a corresponding gradient of ca 59 mV/pH unit (at 25°C) which is consistent with an  $n$  electron,  $m$  proton transfer where  $n$  and  $m$  are likely to be equal to two. By combining the two individual curves in a manner as described in equation [5], a new function (•) is derived with a superior sensitivity for the species to be detected.

20

Analysis of the peak potential as a function of pH at each temperature shows good agreement between the experimental and theoretically predicted values thereby showing the mechanism can be readily used as a simple, inexpensive pH probe, which works over a wide range of temperatures.

30

The novel probe may be placed inside various wellbore tools and installations as described in the following examples.

In FIGs. 8-11 the sensor is shown in various possible downhole applications.

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In FIG. 8, there is shown a formation testing apparatus 810 held on a wireline 812 within a wellbore 814. The apparatus 810 is a well-known modular dynamic tester (MDT, Mark of Schlumberger) as described in the co-owned U.S. Pat. No. 3,859,851 to Urbanosky U.S. Pat. No. 3,780,575 to Urbanosky and Pat. No. 4,994,671 to Safinya et al., with this known tester being modified by introduction of a electro-chemical analyzing sensor 816 as described in detail above (FIG 8). The modular dynamics tester comprises body 820 approximately 30m long and containing a main flowline bus or conduit 822. The analysing tool 816 communicates with the flowline 822 via opening 817. In addition to the novel sensor system 816, the testing apparatus comprises an optical fluid analyser 830 within the lower part of the flowline 822. The flow through the flowline 822 is driven by means of a pump 832 located towards the upper end of the flowline 822. Hydraulic arms 834 and counterarms 835 are attached external to the body 820 and carry a sample probe tip 836 for sampling fluid. The base of the probing tip 836 is isolated from the wellbore 814 by an o-ring 840, or other sealing devices, e.g. packers.

Before completion of a well, the modular dynamics tester is lowered into the well on the wireline 812. After reaching a target depth, i.e., the layer 842 of the formation which is to be sampled, the hydraulic arms 834 are extended to engage the sample probe tip 836 with the formation. The o-ring 840 at the base of the sample probe 836 forms a seal between the side of the wellbore 844 and the formation 842 into which the probe 836 is inserted and prevents the sample probe 136 from acquiring fluid directly from the borehole 814.

Once the sample probe 836 is inserted into the formation 842, an electrical signal is passed down the wireline 812 from the surface so as to start the pump 832 and the sensor systems 816

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and 830 to begin sampling of a sample of fluid from the formation 842. The electro-chemical detector 816 is adapted to measure the pH and ion-content of the formation effluent.

- 5 A bottle (not shown) within the MDT tool may be filled initially with a calibration solution to ensure in-situ (downhole) calibration of sensors. The MDT module may also contain a tank with a greater volume of calibration solution and/or of cleaning solution which may periodically be pumped through the sensor
- 10 volume for cleaning and re-calibration purposes.

Electro-chemical probes in an MDT-type downhole tool may be used for the absolute measurements of downhole parameters which significantly differ from those measured in samples on the

15 surface (such as pH, Eh, dissolved  $H_2S$ ,  $CO_2$ ). This correction of surface values are important for water chemistry model validation.

A further possible application of the novel sensor and

20 separation system is in the field of measurement-while-drilling (MWD). The principle of MWD measurements is known and disclosed in a vast amount of literature, including for example United States Patent No. 5,445,228, entitled "Method and apparatus for formation sampling during the drilling of a hydrocarbon well".

25

In FIG. 9, there is shown a wellbore 911 and the lower part of a drill string 912 including the bottom-hole-assembly (BHA) 910. The BHA carries at its apex the drill bit 913. It includes further drill collars that are used to mount additional

30 equipment such as a telemetry sub 914 and a sensor sub 915. The telemetry sub provides a telemetry link to the surface, for example via mud-pulse telemetry. The sensor sub includes the novel electro-chemical analyzing unit 916 as described above. The analyzing unit 916 collects fluids from the wellbore via a

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small recess 917 protected from debris and other particles by a metal mesh.

During drilling operation wellbore fluid enters the recess 917 and is subsequently analyzed using sensor unit 916. The results are transmitted from the data acquisition unit to the telemetry unit 914, converted into telemetry signals and transmitted to the surface.

10 A third application is illustrated in FIG. 10. It shows a Venturi-type flowmeter 1010, as well known in the industry and described for example in the United States Patent No. 5,736,650. Mounted on production tubing or casing 1012, the flowmeter is installed at a location within the well 1011 with a wired  
15 connection 1013 to the surface following known procedures as disclosed for example in the United States Patent No. 5,829,520.

The flowmeter consists essentially of a constriction or throat 1014 and two pressure taps 1018, 1019 located conventionally at  
20 the entrance and the position of maximum constriction, respectively. Usually the Venturi flowmeter is combined with a densiometer 1015 located further up- or downstream.

The novel electro-chemical analyzing unit 1016 is preferably  
25 located downstream from the Venturi to take advantage of the mixing effect the Venturi has on the flow. A recess 1017 protected by a metal mesh provides an inlet to the unit.

During production wellbore fluid enters the recess 1017 and is  
30 subsequently analyzed using sensor unit 1016. The results are transmitted from the data acquisition unit to the surface via wires 1013.

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Various embodiments and applications of the invention have been described. The descriptions are intended to be illustrative of the present invention. It will be apparent to those skilled in the art that modifications may be made to the invention as

- 5 described without departing from the scope of the claims set out below.

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## CLAIMS

1. An electro-chemical sensor comprising  
at least two redox systems sensitive to the same species.  
5
2. The sensor of claim 1 wherein the species are protons.
3. The sensor of claim 1 wherein the at least two redox systems  
have a maximum redox reaction at different voltages.  
10
4. The sensor of claim 1 wherein the at least two redox systems  
are mounted onto the same conductive substrate.
5. The sensor of claim 1 comprising a detector adapted to  
15 measure the redox potential of said at least two redox  
system in the presence of the species and to convert  
measurements into an signal indicative of the concentration  
of said species.
- 20 6. An electro-chemical sensor for determining the concentration  
of a molecular species in a fluid comprising a first  
redox system sensitive to said species and a second  
redox system sensitive to said species;  
voltage supply and electric current detector to perform  
25 voltammogramic measurements;  
and an analyser to detect relative shifts in said  
voltammogramic measurements.
- 30 7. A downhole tool for measuring characteristic parameters of  
wellbore effluents comprising an electro-chemical sensor in  
accordance with claim 1.
8. A downhole formation sampling tool for measuring  
characteristic parameters of wellbore effluents comprising  
35 an electro-chemical sensor in accordance with claim 1.



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9. A downhole tool for measuring characteristic parameters of wellbore effluents comprising an electro-chemical sensor in accordance with claim 1 mounted onto a permanently installed part of the wellbore.

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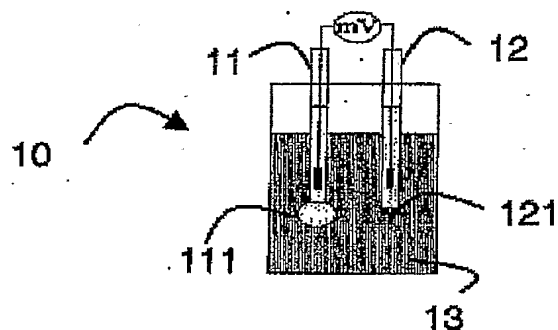
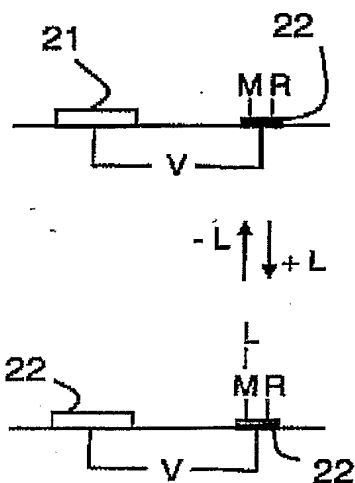
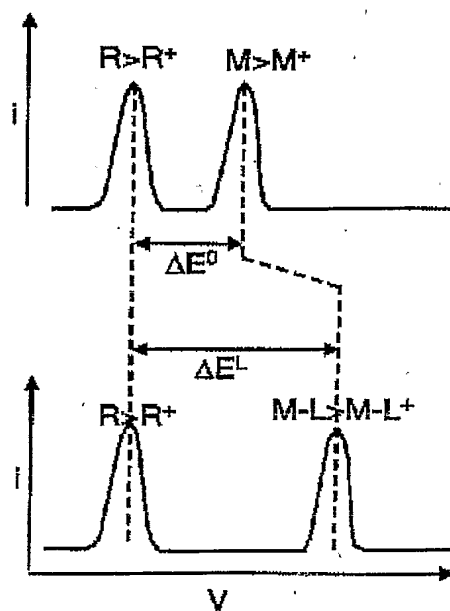
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## ABSTRACT

An electro-chemical sensor is described having two molecular  
5. redox systems sensitive to the same species and having an  
detector to detect relative shifts in the voltammograms of the  
to redox systems.



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FIG. 1  
(Prior Art)FIG. 2A  
(Prior Art)FIG. 2B  
(Prior Art)FIG. 2C  
(Prior Art)



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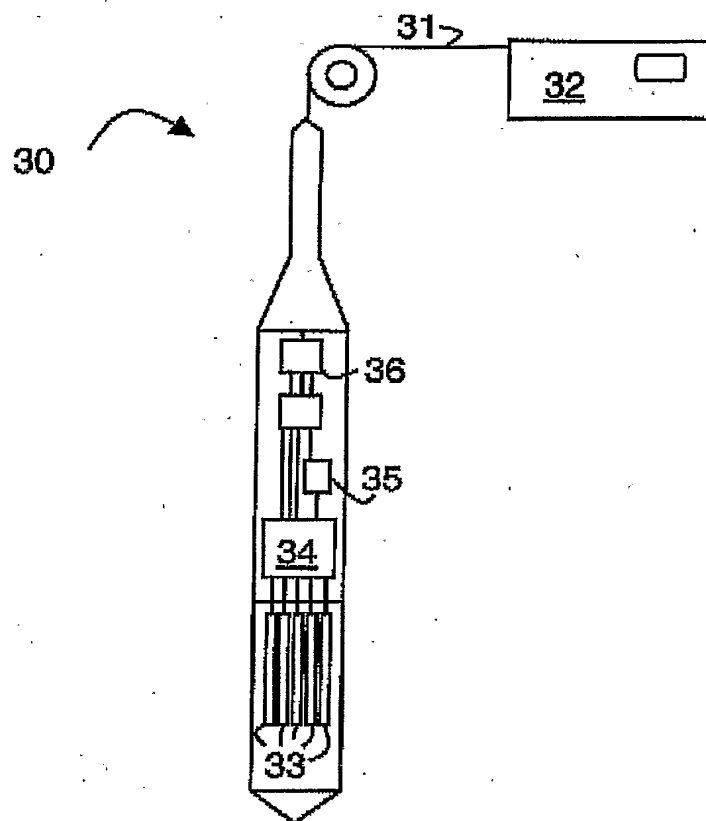


FIG. 3  
(Prior Art)



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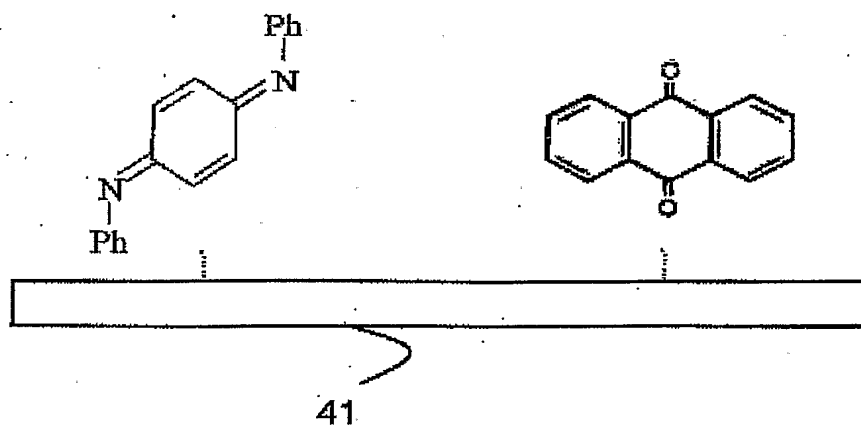


FIG. 4A

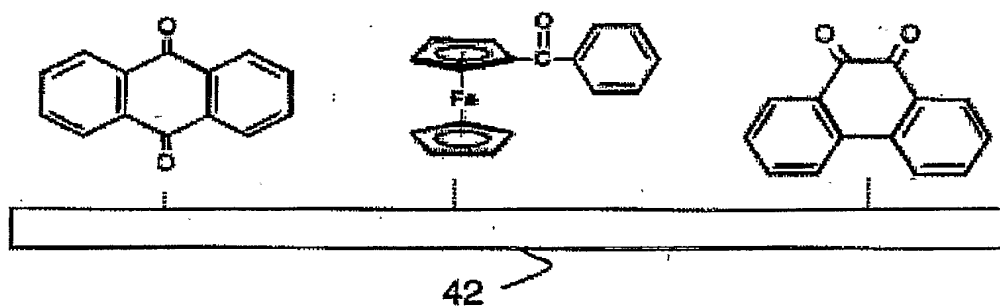


FIG. 4B





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FIG. 4C

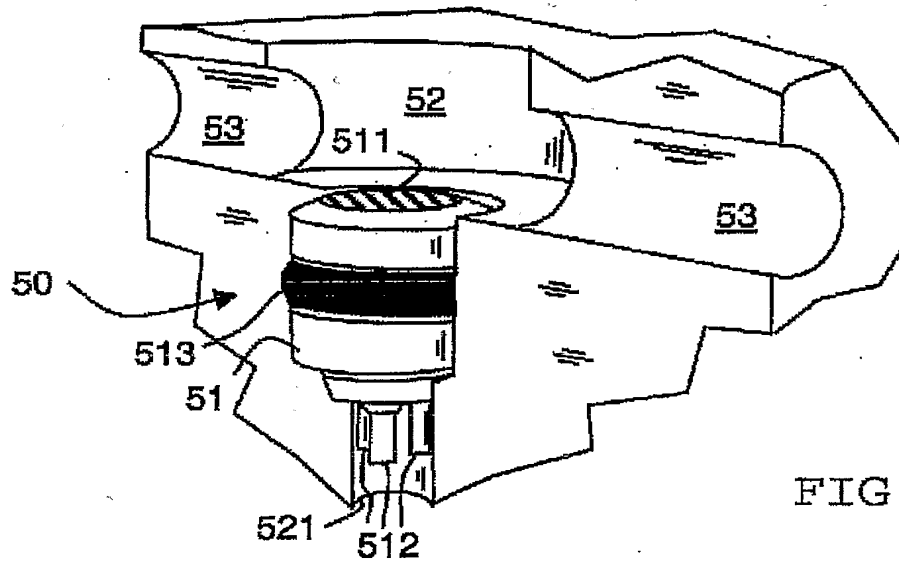
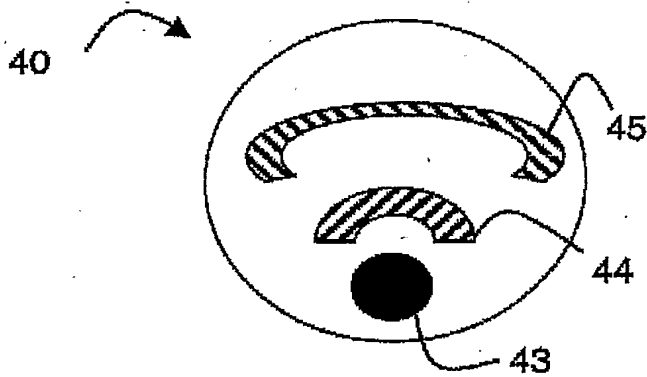


FIG. 5



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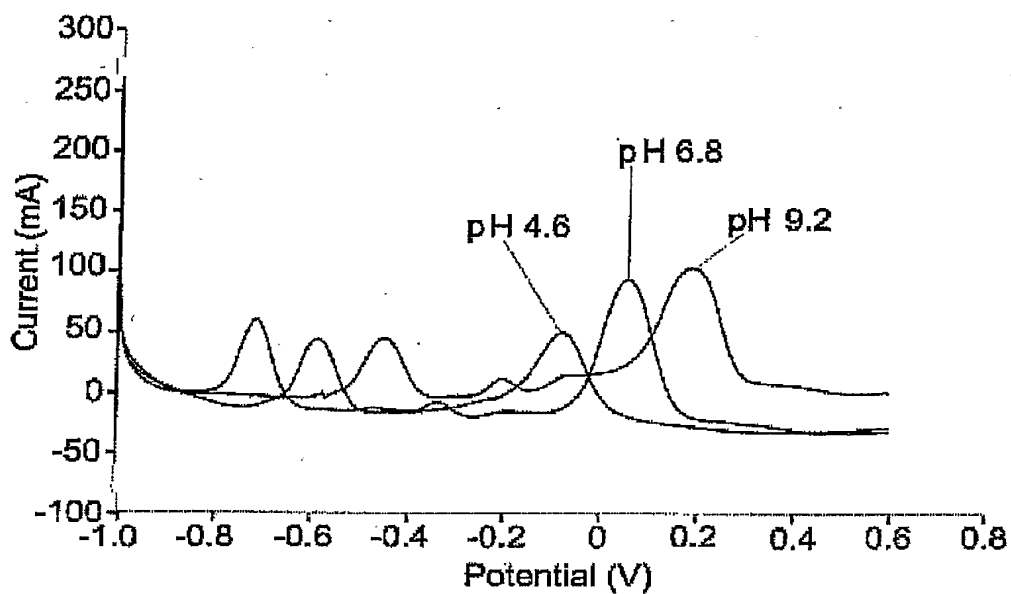


FIG. 6



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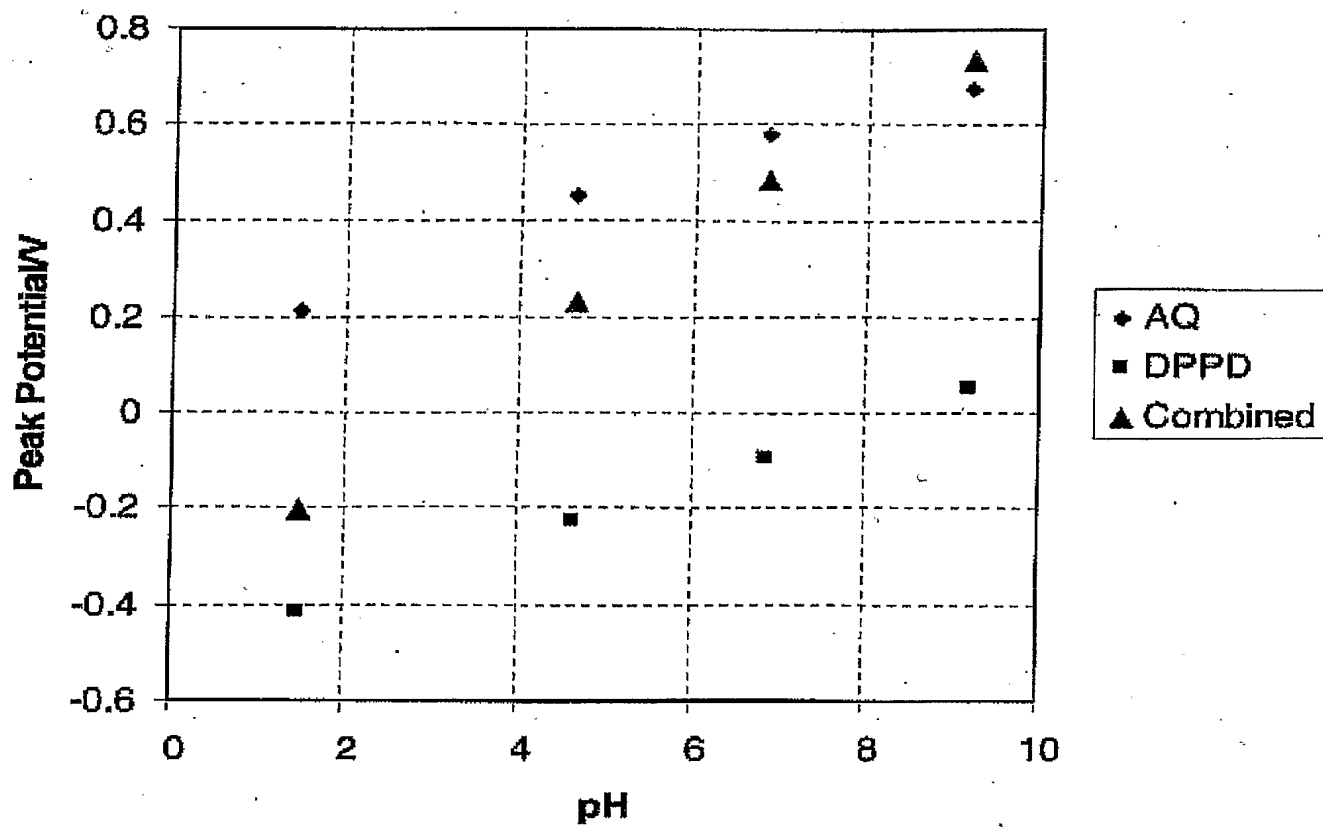
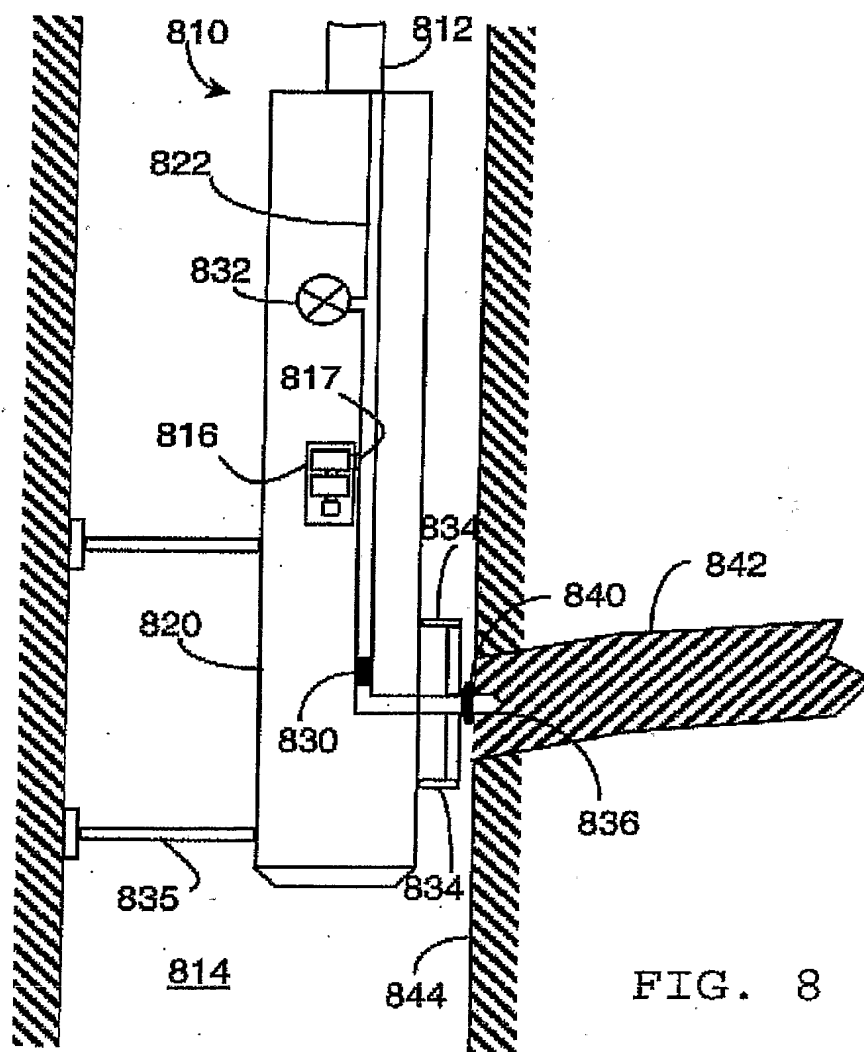


FIG. 7



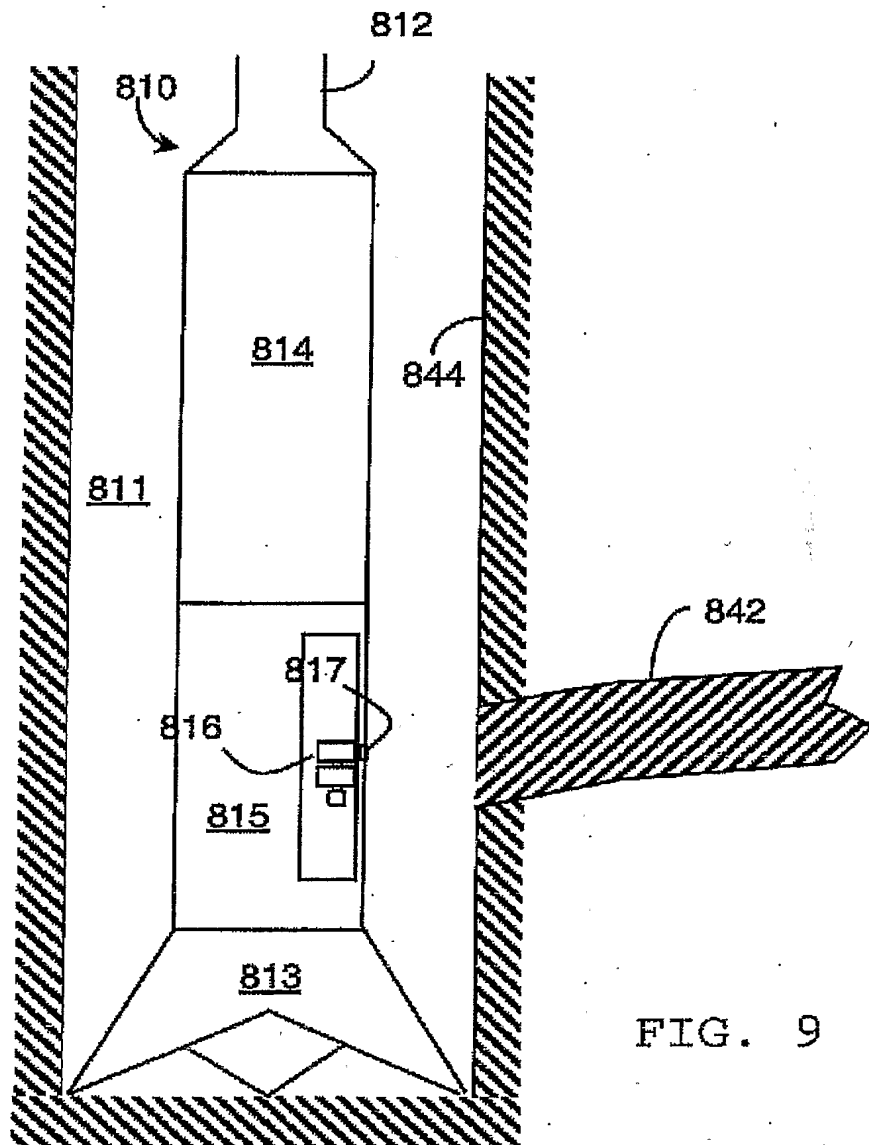
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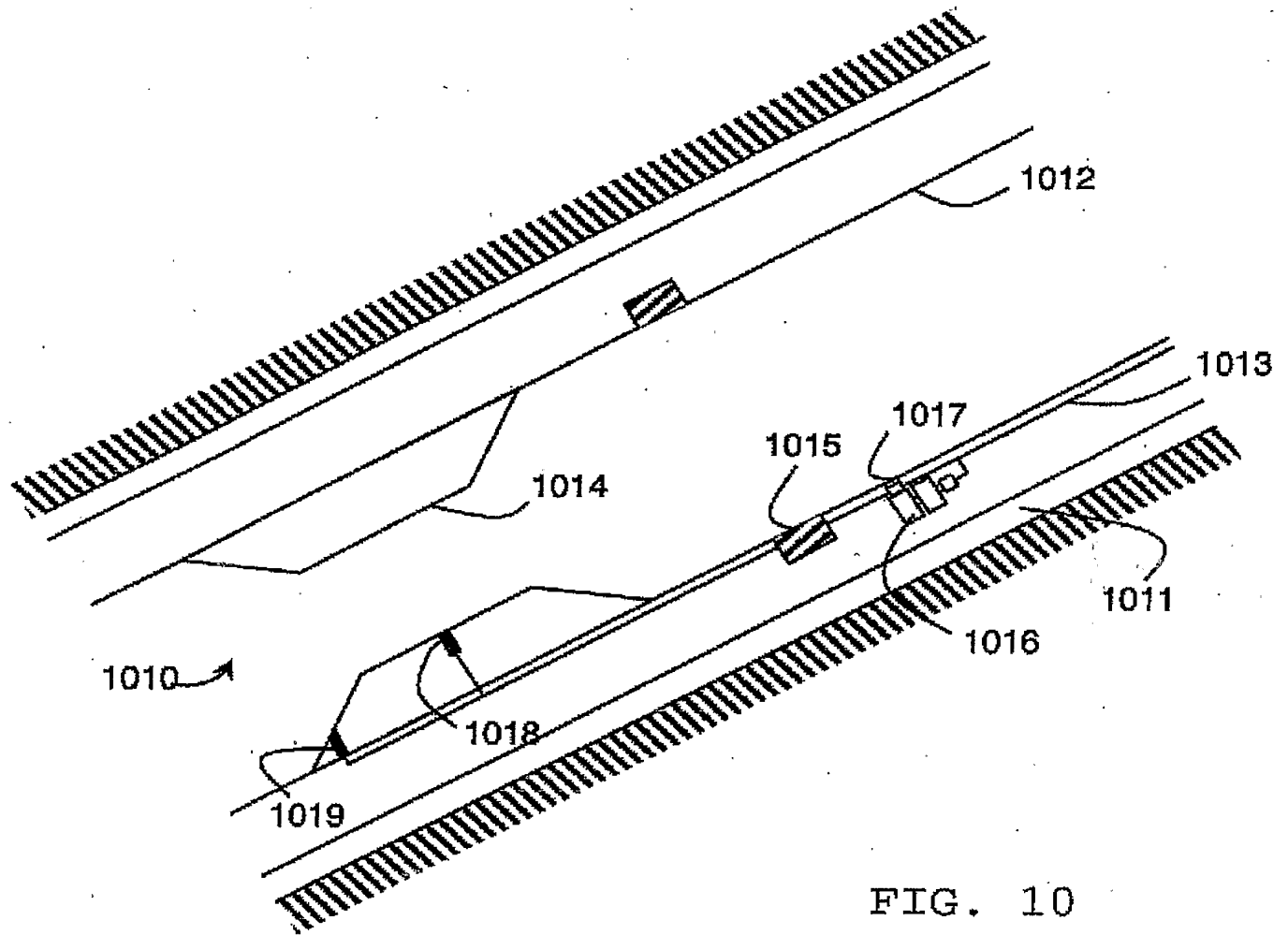


FIG. 10

